Optical activity in the Drude helix model

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(Dated: February 2, 2008)

Abstract

An old classical one-particle helix model for optical activity, first proposed by Drude, is reconsidered here. The quantum Drude model is very instructive because the optical activity can be calculated analytically without further approximations apart from the Rosenfeld long wavelength approximation. While it was generally believed that this model, when treated correctly, is optically inactive, we show that it leads to optical activity when the motion of the particle is quantum mechanically treated. We also find that optical activity arises even in the classical regime at non-zero energy, while for zero energy the model is inactive, in accordance with previous results. The model is compared with other one-electron models and it is shown that its predicted optical activity is qualitatively different from those of other one-electron systems. The vanishing of optical activity in the classical zero-energy limit for the Drude model is due to the localization of the particle at the equilibrium position, whereas in the analogous model of a particle moving freely on a helix without a definite equilibrium position, optical activity does not vanish but the spectrum is rescaled. The model under study leads to interesting predictions about the optical properties of e. g. helicene derivatives.

PACS numbers: 33.55.Ad, 78.20.Ek, 78.20.Bh

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I. INTRODUCTION

Optical activity is of enormous interest in chemistry, e. g. as an analytical tool to determine the absolute configuration of chiral molecules by comparing experimentally obtained optical rotatory dispersion spectra with calculated ones. Only recently quantum chemical ab initio techniques provide sprectra of sufficient accuracy for that purpose [1, 2, 3, 4]. On the other hand, due to their unique optical properties, chiral materials are of interest on their own: Chiral materials belong to the larger class of bi-isotropic or, even more generally, bi-anisotropic materials [5, 6, 7]. Especially interesting in this context [8] are materials whose electric susceptibility and magnetic permeability are both negative in a given frequency range. Meta-materials for the use in the microwave region consisting of helical structures have been studied as promising candidates both experimentally [9, 10, 11] and theoretically [12, 13, 14]. For applications working in the visible range, one has to pass to a molecular level. There, quite different classes of molecules with helical structure show strong optical activity [15, 16, 17, 18, 19, 20, 21].

For the optimization of these properties, ab initio calculations are only of limited value as they do not show explicitly the dependence of the properties on the variables of the system. On the other hand many model systems [22, 23, 24, 25, 26, 27] have been devised whose optical activity can be calculated analytically as a function of their parameters.

In the following, we will be interested in modelling the optical activity of helical molecules. An especially simple model, which can be solved analytically, is the one-electron model[1] for free motion on a helix as proposed by Tinoco and Woody [25]. It was applied [28] to describe the ORD spectrum of hexahelicene [15], a helix shaped molecule built up of six annellated benzene rings. The model assumed a box shaped potential, which is zero inside the molecule and infinite outside. However, this implied degeneracy of all positions inside the molecule is questionable and instable with respect to perturbations. More recently, helicene derivatives like helicenebisquinones [17, 18] and tetrathiahelicenes [19] have been shown to have very large second order non-linear responses making them interesting materials for non-linear optics. For these helicene derivatives, the assumption of free motion along the helix cannot be justified any more. Maki and Persoons [29] instead have assumed that

[1] It is important that the one-electron models studied in this article can be used to descibe also systems of many electrons when these are treated as independent particles.

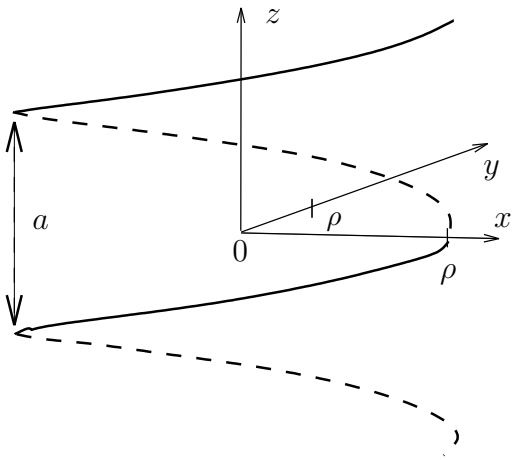

FIG. 1: The spiral considered by Drude with radius ρ and pitch a.

the electronic motion along the helix is controlled by an effective harmonic potential. This model probably is historically the first,—it was proposed by Paul Drude [22] in 1900—, to explain the phenomenon optical activity. Astonishingly, it has never been treated quantum mechanically, probably because it was believed that the original classical model is optically inactive. We will show, however, that this holds true only at zero energy.

Drude considered the motion of a single classical charged particle with charge e and mass m_e constrained to move on a helical path so that $x(t) = \rho\cos\phi(t)$, $y(t) = \rho\sin\phi(t)$, and $z(t) = a/(2\pi)\phi(t)$. Here ρ is the radius of the helix and a is the pitch (cf. fig. 1). The helix may be either right or left handed, depending on the sign of a. The motion of the particle is governed by the harmonic Hamiltonian

$$H(\phi(t), p_\phi(t)) = \frac{1}{2M}p_\phi^2(t) + \frac{M\Omega^2}{2}\phi^2(t), \tag{1}$$

with Ω being the frequency. The canonical momentum $p_\phi(t)$ is

$$p_\phi(t) = \frac{\partial}{\partial\dot{\phi}(t)}\left(\frac{1}{2}m_e\dot{\mathbf{x}}^2(t)\right) = M\dot{\phi}(t), \tag{2}$$

with the moment of inertia $M = m_e(\rho^2 + a^2/(2\pi)^2)$ and the vector $\mathbf{x}(t) = (x(t), y(t), z(t))^T$. Drude considered the forced motion of the charged particle under the influence of the external electric or magnetic fields of a polarized wave and calculated the resulting electric and magnetic polarization. He found a rotation of the plane of polarization. In the following

it becomes important that Drude considered forced oscillations, only, and did not take into account any free oscillations. Hence, the unperturbed system is frozen in at its equilibrium position and has zero energy.

This model was used extensively in the years following its proposal to describe optical rotation spectra although soon alternative many particle models, like the coupled oscillator model, were propagated [30]. In 1933, however, Walther Kuhn [31] showed that the optical activity of the helix model was an artifact due to a physically unjustified assumption made by Drude who took only into account the electric (magnetic) moment parallel to the axis induced by a magnetic (electric) field component parallel to the axis, while it neglected the electric (magnetic) moments perpendicular to the axis induced by a perpendicular magnetic (electric) field. We will speak in the following of the parallel and perpendicular component of optical activity. So, while Drude only considered the parallel component of optical activity, Kuhn showed that the parallel and perpendicular components of optical activities cancel in an isotropic ensemble in the regime of classical mechanics at zero energy.

Some years afterwards, Condon, Altar and Eyring [24] presented an alternative quantum mechanical one-particle model which was optically active. However, they made no attempt to explain why the Drude model did not show optical activity. They found that in the classical limit their model also shows optical activity, but failed to notice that this activity vanishes at zero energy, too, because it is proportional to the mean quadratic displacement from the equilibrium position of the particle.

The Drude model was then long forgotten until Desobry and Kabir [32] showed in the seventies that the Drude model exhibits optical activity in the nonlinear regime. However, they did not attempt to solve the Drude model quantum mechanically, neither did they consider the behavior at finite energies.

For the related problem of free motion on a helix, Tinoco and Woody [25] already established a non-vanishing optical activity in the quantum regime. While the latter model is formally very similar to the Drude model, the two models' behavior at low energies is quite distinct as the particle will become localized at the equilibrium position in the Drude model while there is no equilibrium position in the case of free motion.

The outline of this article is the following:

In sec. II we will determine the quantum mechanical expression for the rotational strength of the Drude model which determines both the optical rotatory power and the circular

dichroism of the model.

In sec. III we will derive two expansions of the general result: In the first case, we will expand the optical activity into a series in $\hbar$ at zero energy. In the second case, we expand into a series in E at $\hbar = 0$, the classical limit. Furthermore, the optical activity of an oriented sample of helices will be derived.

In sec. IV we will compare the optical activity of the Drude model with that of the model of Condon, Altar, and Eyring on the one hand and that of the model of free motion on a helix of Tinoco and Woody on the other.

Finally, a conclusion will be given in sec. V.

II. ROTATIONAL STRENGTH OF THE QUANTUM DRUDE MODEL.

To determine the optical activity of the Drude helix model we start from an expression for the rotation Φ in radians per centimeter due to Rosenfeld [33]

$$\Phi = \frac{8\pi}{3c\hbar} N_1 \frac{\tilde{n}^2 + 2}{3} \sum_n \rho_n \sum_m \frac{\omega^2 R_{mn}}{\omega_{mn}^2 - \omega^2} \tag{3}$$

where $R_{mn} = \Im\{\langle n|\mathbf{d}|m\rangle \cdot \langle m|\mathbf{m}|n\rangle\}$ is the rotational strength and $\omega_{mn} = (E_m - E_n)/\hbar$ are the eigen-frequencies of the system. The particle density is N_1, the index of refraction is $\tilde{n}$, while ρ_n is a statistical weight. The operator of the electric and magnetic dipole moment, respectively, is $\mathbf{d} = e\,\mathbf{x}$ and $\mathbf{m} = \frac{e}{2m_e c}\mathbf{L} = \frac{e}{2m_e c}\mathbf{x} \times \mathbf{p}$. The problem to determine of the optical activity thus reduces to the evaluation of the rotational strength R_{mn}. Addition of an infinitesimal imaginary part $\omega \to \omega + i\epsilon$ to the frequency in expression 3 removes the singularities at $\omega = \omega_{mn}$ and at the same time, the rotation Φ acquires an imaginary part upon this substitution which can be shown to correspond to the circular dichroism of the transition from state n to state m. Using the well known formula $\lim_{\epsilon\to 0}(x + i\epsilon)^{-1} = \mathrm{P}(x^{-1}) - i\pi\delta(x)$, where $\mathrm{P}(x^{-1})$ means the principal part, it is easy to show that the circular dichroism spectrum consists of lines centered at the frequencies ω_{mn}.

The position of a particle on a helix is described by only one parameter ϕ. While in classical mechanics it is straightforward to find the corresponding momentum p_ϕ, in quantum mechanics [34, 35] one has to specify much more carefully how the (approximate) restriction to the one-dimensional sub-manifold,—in our case a helix—, is achieved before the corresponding operators ϕ, p_ϕ and their commutation relations can be found. For the special

case of the motion on a helix, there exists a very simple recipe [25] for quantization: it can be shown that the operator p_ϕ fulfills a canonical commutation relation with ϕ, $[p_\phi, \phi] = \frac{\hbar}{i}$, whence $p_\phi = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$ so that the hamiltonian 1 is easily quantized.

The position operator is formally identical to the classical expression,

$$\mathbf{x} = \rho\left(\cos\phi, \sin\phi, \frac{a}{2\pi\rho}\phi\right)^T. \tag{4}$$

The cartesian momentum operator $\mathbf{p}$ can be expressed by the time derivative of $\mathbf{x}$, $\mathbf{p} = m_e\dot{\mathbf{x}}$. As the general expression for the time derivative of an operator A depending only on ϕ but not on p_ϕ is $\dot{A} = \frac{i}{\hbar}[H, A] = 1/2\{\dot{\phi}, \frac{\partial A}{\partial\phi}\}$, we may derive an explicit expression for $\mathbf{p}$ and finally for the angular momentum operator $\mathbf{L} = \mathbf{x} \times \mathbf{p}$. Actually, it can be shown that in case of the Drude model the operator $\mathbf{L}$ itself may be expressed as the time derivative of an "angle" vector $\mathbf{W}$ which depends on ϕ, only, $\mathbf{L} = \frac{i}{\hbar}[H, W]\frac{m_e\rho a}{2\pi}$. The explicit expression for $\mathbf{W}$ being

$$\mathbf{W} = \left(-2\cos\phi - \phi\sin\phi, -2\sin\phi + \phi\cos\phi, \frac{2\pi\rho}{a}\phi\right)^T. \tag{5}$$

Hence, the rotational strength becomes

$$\begin{aligned} R_{mn} &= \frac{e^2}{2m_e c}\frac{m_e\rho a}{2\pi}\Im\{\langle n|\mathbf{x}|m\rangle \cdot \langle m|\frac{i}{\hbar}[H, \mathbf{W}]|n\rangle\} \\ &= \omega_{mn}\frac{e^2\rho a}{8\pi c}\Re\{\langle n|\mathbf{x}|m\rangle \cdot \langle m|\mathbf{W}|n\rangle\} \\ &= \omega_{mn}\frac{e^2\rho a}{16\pi c}\{\langle n|\mathbf{x}|m\rangle \cdot \langle m|\mathbf{W}|n\rangle + \langle n|\mathbf{W}|m\rangle \cdot \langle m|\mathbf{x}|n\rangle\}, \end{aligned} \tag{6}$$

where we have assumed the functions $\psi_{n,m}(\phi)$ to be real valued in the last line.

Introducing the vector

$$\mathbf{K} = \left(\gamma^{-2}\cos\gamma\phi, \gamma^{-2}\sin\gamma\phi, \gamma\phi\right)^T, \tag{7}$$

we may write the rotational strength in a more symmetrical form

$$R_{mn} = \omega_{mn}\frac{e^2\rho^2 a}{8\pi c}\left(\frac{\partial}{\partial\gamma}|\langle n|K|m\rangle|^2\right)_{\gamma=1} \tag{8}$$

which is easily shown to hold true. This expression can be simplified further to give

$$\begin{aligned} R_{mn} = \omega_{mn}\frac{e^2\rho^2 a}{8\pi c}\times \\ \times\left(\frac{\partial}{\partial\gamma}\left(\gamma^{-4}|\langle n|e^{i\gamma\phi}|m\rangle|^2 + |\langle n|\gamma\phi|m\rangle|^2\right)_{\gamma=1}\right). \end{aligned} \tag{9}$$

Up to now, the form of the functions $\psi_{n/m}(\phi)$ or the dependence of ω_{mn} on m and n was not of relevance, whence we can use formula 9 to calculate not only the optical activity of the Drude model but also e. g. that for free motion on a helix with given winding number which should allow to reproduce the results of Tinoco and Woody [25]. In case of the Drude model the states of the system are characterized by the single quantum number n so that $E_n = \hbar n\Omega$. The appearing matrix elements are well known [36],

$$\langle n|e^{i\gamma\phi}|m\rangle = e^{\lambda^2/2}\sqrt{\frac{N!}{(N+K)!}}\lambda^K L_N^K(-\lambda^2) \tag{10}$$

with $\lambda = i\gamma\sqrt{\hbar/(2M\Omega)}$, $N = \min(m,n)$, and $K = |m-n|$. The L_N^K are Laguerre polynomials,

$$L_N^K(x) = \sum_{j=0}^{K}\binom{N+K}{N-j}\frac{(-x)^j}{j!}. \tag{11}$$

Also, $|\langle n|\gamma\phi|m\rangle|^2 = \gamma^2\frac{\hbar}{2M\Omega}(N+K)\delta_{K,1}$ with the Kröneker symbol $\delta_{i,j} = 1$ for $i = j$ and $\delta_{i,j} = 0$ for $i \neq j$.

Finally, we find the following expression for the rotational strength of the Drude model,

$$R_{mn} = \omega_{mn}\frac{e^2\rho^2 a}{8\pi c}\left(\frac{\partial}{\partial\gamma}\left(\gamma^{-4}\left(\gamma^2\frac{\hbar}{2M\Omega}\right)^K e^{-\gamma^2\frac{\hbar}{M\Omega}}\frac{N!}{(N+K)!}\left(L_N^K\left(\gamma^2\frac{\hbar}{2M\Omega}\right)\right)^2 + \right.\right.$$
$$\left.\left. + \gamma^2\frac{\hbar}{2M\Omega}(N+K)\delta_{K,1}\right)_{\gamma=1}\right). \tag{12}$$

Exploiting the relation $\frac{\partial}{\partial x}L_N^K(x) = (-1)L_{N-1}^{K+1}(x)$, the derivation with respect to γ may easily be carried out.

III. CLASSICAL AND LOW ENERGY LIMITS OF THE OPTICAL ACTIVITY AND OPTICAL ACTIVITY OF ORIENTED HELICES.

We will now consider two limiting cases of that general expression. The first one is the classical limit. The second limit is the low energy limit in which only the ground state ($n = 0$) is occupied. The combined classical and $E = 0$ limit was considered by Drude and Kuhn and it is interesting to explore why and how the optical activity tends to zero with $\hbar$ and E.

In the classical limit, the quantum number n tends to infinity as $\hbar$ tends to 0 while the energy E is hold fixed. Radiative transitions will only be observed between states with

quantum numbers n and m such that K is a small number. Hence, ΔE tends to zero and energy becomes a continuous function of time $E = E_n \approx E_m$ to order $\mathrm{O}(\hbar^0)$. The classical motion will be periodic with period Ω. Furthermore, the observed transition frequencies will become multiples of this fundamental frequency, $\omega_{mn} = \pm K\Omega$, as is well known from the correspondence principle [37]. We will eliminate $\hbar$ in favor of N and E from eq. 10, $\hbar = E/(N\Omega)$.

In this limit (cf. ref. [38], eq. 22.15.2) the Laguerre polynomials approach Bessel functions, $\lim_{N\to\infty} N^{-K} L_N^K(x/N) = x^{-K/2} J_K(2\sqrt{x})$. To apply the last formula to our problem we write $-\lambda^2 = \gamma^2 \frac{E}{2M\Omega^2}/N$ so that finally

$$R_{mn} = \frac{e^2\rho^2 aK\Omega}{8\pi c}\frac{\partial}{\partial\gamma}\left(\gamma^{-4} J_K^2\left(2\gamma\sqrt{\frac{E}{2M\Omega^2}}\right) + \right. \\ \left. + \gamma^2 \frac{E}{2M\Omega^2}\delta_{K,1}\right) + \mathrm{O}(\hbar). \quad (13)$$

In the following, we will call R_{mn} alternatively $R_K(E,\Omega)$. We are still not done in deriving the classical limit of eq. 3 as this equation contains a pre-factor $\hbar^{-1}$. In the classical limit, always a large number of quantum states is occupied so that we have to specify the function ρ_n. E. g. we may assume a micro-canonical distribution in which only states in a small energy range from E to $E + dE$ are occupied. For all $n = E/(\hbar\Omega)$ in that range we have $\rho_n = \hbar\Omega/dE$. If both states n and m are inside the interval dE then, as $R_{m,n} = -R_{n,m}$, the contribution of these states will cancel. Trivially, if both n and m are outside the interval, $R_{mn} = 0$, too. Only the K states with n inside the interval and m outside (or vice versa) will make a non-vanishing contribution so that

$$\sum_n \sum_m \frac{\rho_n R_{mn}\omega^2}{\omega_{mn}^2 - \omega^2} = \\ \rho_N \sum_K \frac{K\omega^2}{K^2\Omega^2 - \omega^2}\{R_K(E+dE,\Omega) - R_K(E,\Omega)\} = \\ \hbar\Omega \sum_K \frac{K\omega^2}{K^2\Omega^2 - \omega^2}\frac{\partial R_K(E,\Omega)}{\partial E}, \quad (14)$$

whence the classical analog of the Rosenfeld formula becomes

$$\Phi^{\mathrm{class}} = \frac{8\pi}{3c} N_1 \frac{\tilde{n}^2 + 2}{3} \sum_K \frac{\omega^2}{K^2\Omega^2 - \omega^2} K\Omega \frac{\partial R_K(E,\Omega)}{\partial E}. \quad (15)$$

This formula will not only hold true in case of the harmonic oscillator. In general, Ω will then be a function of E, too.

Expression 13 depends on E only in the combination $E/(M\Omega^2) = \langle\phi^2\rangle$, which is the mean quadratic fluctuation of the angle ϕ. For small values of E, we may use the Taylor expansion of the Bessel function to find the expansion of $R_K(E)$ into a series in E. The first non-vanishing term in that series is of order $\mathrm{O}(E^2)$,

$$\Phi^{\mathrm{class}} = \frac{e^2\rho^2 a N_1}{3Mc^2}\frac{\tilde{n}^2+2}{3}\left(\frac{E}{2M\Omega^2}\right)^2 \sum_K \frac{K^2\omega^2}{K^2\Omega^2-\omega^2}\left(\frac{5}{4}\delta_{K,1}-\frac{1}{2}\delta_{K,2}+\frac{1}{12}\delta_{K,3}\right)+\mathrm{O}(E^3), \tag{16}$$

correspondingly, there are three lines in the circular dichroism spectrum at $\omega = \Omega$, 2Ω, and 3Ω.

In experiments, probably the only distribution that may be realizable in an ensemble is the canonical distribution $\rho_n = \exp(-\beta E_n)/\{\sum_m \exp(-\beta E_m)\}$ with $\beta = 1/(kT)$ where T is the temperature. In the classical limit, where E_n becomes continuous, the transition from the micro-canonical optical activity 16 to the canonical corresponds to a Laplace transform which specializes to the replacement of E^2 in eq. 16 by $2(kT)^2$. We see that the optical activity will thaw up proportional to T^2

The second interesting limiting case is that of zero energy when all the systems are in their ground states. The corresponding expression for the rotational strength R_{0m} is considerably simpler than the general expression 12, as $L_0^K(x) = 1$. We may expand this result into a series in $\hbar$ to find the lowest order correction to the classical optical activity from which we already know that it vanishes. We find that also the first order correction in $\hbar$ vanishes, too. The second order result reads

$$\frac{R_{m0}}{\hbar} = \frac{e^2\rho^2 a}{4\pi c\hbar}\left(\frac{\hbar}{2M\Omega}\right)^3\left(2\delta_{K,1}-\delta_{K,2}+\frac{1}{6}\delta_{K,3}\right)+\mathrm{O}(\hbar^3). \tag{17}$$

Again, the circular dichroism spectrum will consist in lowest order of three lines centered at the fundamental frequency Ω and its first and second harmonic.

We may compare this result to the prediction that would arise if we would start like Drude from the physically unjustified approximation of considering the parallel component of optical activity, $R_{mn} \approx R_{mn}^{\parallel} = \Im\{\langle n|d_z|m\rangle\langle m|m_z|n\rangle\} = \omega_{mn}\frac{e^2}{4mc}\frac{m\rho^2 a}{2\pi}\frac{\partial}{\partial\gamma}(|\langle n|\gamma\phi|m\rangle|^2|)_{\gamma=1}$, only. The correct result, eq. 9, can be seen to be a sum of two terms, $R_{mn} = R_{mn}^{\perp} + R_{mn}^{\parallel}$ with $R_{mn}^{\perp} = \omega_{mn}\frac{e^2}{4mc}\frac{m\rho^2 a}{2\pi}\frac{\partial}{\partial\gamma}(\gamma^{-4}|\langle n|e^{i\gamma\phi}|m\rangle|^2)|_{\gamma=1}$. Hence, the optical rotation in the Drude

approximation is

$$\Phi_{\parallel} = \frac{e^2\rho^2 a}{3c^2 M} N_1 \frac{\tilde{n}^2+2}{3} \frac{\omega^2}{\Omega^2-\omega^2}. \tag{18}$$

This expression for the optical activity does not depend on $\hbar$ nor on E, furthermore, the response of the system would always be linear for any strength of the driving field.

We infer that at zero energy and in the linear and classical regime, the parallel and the perpendicular components of optical activities cancel. When the extension of the wave-functions increases, either due to quantum effects, due to non-zero kinetic energy of the unperturbed system, or when the field strength is increased, the perpendicular response will become an-harmonic and a net optical rotation will arise.

Kauzman [39] noted that a two electron system in which the electrons are correlated so that their position ϕ differs always by 180° will show a specific rotation as predicted by eq. 18. It is not difficult to convince oneself that in this model the perpendicular responses of the two electrons mutually cancel.

These considerations lead naturally to the consideration of the optical activity of an oriented sample of helices. A nice example of such a system which has been studied experimentally [17, 18] is a Langmuir-Blodgett film composed of supramolecular arrays of helicene derivatives.

As a sample of parallel oriented helices will be an uniaxial system, optical rotation will only be observed, if the propagation vector of light is parallel to the axis of the helices. In this case both the electric and magnetic field will be perpendicular to the propagation vector of light, so that one might expect that the optical activity is determined by the component $R^{\perp}_{mn}$. In fact, this is not entirely true, as there are also contributions [27] which are due to interference of electric dipole transitions with electric quadrupole transitions so that

$$R^{\text{axial}}_{mn} = \frac{\omega_{mn}}{3c}\Re\{\langle m|d_y|m\rangle\langle m|\Theta_{xz}|n\rangle - \langle m|d_x|m\rangle\langle m|\Theta_{yz}|n\rangle\} + \\ + \Im\{\langle m|d_x|m\rangle\langle m|m_x|n\rangle + \langle m|d_y|m\rangle\langle m|m_y|n\rangle\}. \tag{19}$$

Here, $d_{x,y}$ and $m_{x,y}$ are the x- and y-components, respectively, of the electric and magnetic dipole moment vector $\mathbf{d}$ and $\mathbf{m}$ while $\Theta_{xz} = \frac{3e}{2}xz$ and $\Theta_{yz} = \frac{3e}{2}yz$ are components of the tensor of the electric quadrupole moment. In the second line of eq. 19 we recognize the contribution $R^{\perp}_{mn}$, already defined. The additional contribution due to the quadrupole

moments is easily calculated. As a final result we find

$$R_{mn}^{\text{axial}} = \omega_{mn} \frac{a}{2\pi c} \{ |\langle n|d_x|m\rangle|^2 + |\langle n|d_y|m\rangle|^2 \}. \tag{20}$$

On the other hand, the absorption of the sample due to electric dipole transitions is proportional to $\omega_{mn} f_{mn}^{\text{axial}}$ with the oscillator strength $f_{mn}^{\text{axial}} = \frac{4\pi^2 m_e}{e^2 \hbar} \{ |\langle n|d_x|m\rangle|^2 + |\langle n|d_y|m\rangle|^2 \}$. It is astonishing that e. g. the circular dichroism and the absorption are directly proportional to each other with the proportionality constant being a measure of the chirality of the helices. Furthermore, this result is independent of the potential seen by the charged particle, whence it holds both for the Drude model and for the model of free motion on a helix. It would be interesting to test this prediction for the helicene systems mentioned above [17, 18] for which the classical Drude model has already proven usefull for the calculation of the second-order optical response [29]. We also note that the optical activity will not vanish for an oriented sample, not even in the classical limit at $E = 0$.

IV. COMPARISON WITH OTHER ONE-PARTICLE MODELS

We would like to compare the Drude model with two other one-particle models for optical activity, the model of Condon, Altar, and Eyring on the one hand side and the model of free motion on a helix with finite length on the other. As the quantum mechanical expression for arbitrary quantum numbers is complex on the one hand but lacks specific features on the other we will concentrate in our analysis on the classical and low energy limit.

The model of Condon, Altar, and Eyring assumes that the particle moves in a potential of the form $V = \frac{1}{2}(k_1 x_1^2 + k^2 x_2^2 + k_3 x_3^2) + A x_1 x_2 x_3$ with he k_i are force constants and A controls the strength of the cubic anharmonicity. Condon et al. did solve this model quantum mechanically treating the cubic anharmonicity as a perturbation. They found that the optical activity of the system is proportional to the quadratic amplitudes of oscillation $\langle x_i^2 \rangle$ along the main axes of the unperturbed harmonic oscillator. In the classical limit these amplitudes will tend linearly to zero when the energy goes to zero. As any analytic potential may be expanded into a Taylor series of the assumed form around the equilibrium position and as in the classical limit at small energies the motion of the particle will explore only a small region around the equilibrium position, the response of generic classical systems at low energies will be given by the result derived by Condon et al.

The vanishing of the optical activity as $E \to 0$ is easily understood as the amplitudes of oscillation $\langle |x_i| \rangle$ are proportional to $\sqrt{E}$. At sufficiently small energies the motion of the particle will be nearly harmonic with the influence of the cubic anharmonicity, which is responsible for the optical activity, becoming less and less important as energy is lowered. This conclusion will not only hold true for isotropic samples but also for oriented systems as for quantum motion within a potential quadratic in Cartesian co-ordinates, electric and magnetic dipole (or electric quadrupole) transitions are never allowed simultaneously between any two states. This line of argumentation clearly will not hold for the motion being restricted to the helical path as in the case of the Drude model as the potential is not analytic. Although in the Drude model the motion along the helix is harmonic, electric and magnetic dipole transitions are possible at the same time between two given states as the co-ordinate ϕ does parameterize a curved path.

To understand the vanishing of the optical activity in the classical limit in case of the Drude model we expand $\exp(i\gamma\phi)$, which appears in eq. 9, into a Taylor series. At zero energy we are left with matrix elements $\langle M|\phi^k|0\rangle \sim \hbar^{k/2}$, whence to lowest order in $\hbar$ we find

$$\gamma^{-4}|\langle M|\exp(i\gamma\phi)|0\rangle|^2 \sim \gamma^{-2}|\langle M|\phi|0\rangle|^2 + \mathrm{O}(\hbar^2) \tag{21}$$

so that the first and second term in eq. 9 cancel. As in case of the model of Condon et al., the vanishing of optical activity is due to the strong localization of the position of the particle in the classical low energy limit. We saw already in the preceeding section when discussing the original prediction of Drude that an ensemble of oriented helices will show optical activity even in the classical zero-energy limit. Furthermore, we remark that, as in the semiclassical low energy limit, the extension of the particle's wavefunction will always tend to zero, the use of the Rosenfeld long wavelength approximation will automatically be justified.The free motion of a charged particle on a helix of finite extension is quite different in character from the two models just discussed, as, even in the combined classical and low energy limit, the particle will not become localized as a unique equilibrium position is lacking. Hence, we expect that optical activity will not vanish in the classical limit at $E = 0$. The expression for the optical activity is more complicated than that of the Drude model, as circular dichroism is not only to be expected at multiples of one frequency Ω but at all frequencies $\omega_{mn} = \frac{\hbar\pi^2}{2M\phi_{\max}^2}(m^2 - n^2)$ with $n, m \in [1, \infty]$ and $0 < \phi < \phi_{\max}$. The rotatory power of this model was calculated by Tinoco and Woody [25]. The energy

corresponding to the level n being $E_n = \hbar^2 n^2 \pi^2/(2M\phi_{\max}^2)$, we obtain the classical limit substituting $m^2 + n^2 = 16Mt^2E/\hbar^2$ and $m^2 - n^2 = \frac{8Mt^2}{\hbar} K\Omega(E)$ (again, $K = m - n$) with $\Omega(E) = \sqrt{E}/(2t\sqrt{2M})$ and dropping terms of higher order than $\mathrm{O}(\hbar^0)$. Here, $t = \phi_{\max}/2\pi$ is the winding number of the helix. The resulting expression for the classical rotatory power is of the form $R_{mn} = MK\Omega f(E/(MK^2\Omega^2))$. If we insert this into eq. 15 we notice that the appearing combination $K\Omega(\partial R_K(E,\Omega))/(\partial E)$ is actually independent of E. The only energy dependence enters through the frequency factor $\omega^2/(K^2\Omega^2 - \omega^2)$. Hence, a change in energy will only scale the spectrum or, to put it differently, the optical rotatory dispersion and circular dichroism spectra will be invariant if ω is measured in units of Ω. The vanishing of the optical activity in the models of Drude and Condon et al. is not paralleled by the model of free motion on a helix.

V. CONCLUSION

In sec. II we derived a quantum mechanical expression for the optical rotatory strength of the Drude helix model. The key result of this calculation is eq. 12. We found that the Drude model is optical active in general, with exception of the classical limit at zero energy where the optical activity vanishes. Incidentally, this was just the limit analyzed by Drude [22] and Kuhn [31]. To understand better the reason why optical activity vanishes in that limit, in sec. III we found an expression for the classical optical activity as a function of E (eq. 15). We found that optical activity thaws up like E^2 in the classical limit, a behavior that could have been predicted in principle already by Drude or Kuhn. Similarly, an expansion of the general result in powers of $\hbar$ for $E = 0$ revealed that there are non-vanishing quantum corrections of order $\hbar^2$ to the classical behavior.

While in the general case, the circular dichroism spectrum will consist of lines at any multiple of the fundamental frequency Ω, in both limits $E \to 0$ at $\hbar = 0$ and $\hbar \to 0$ at $E = 0$, respectively, only lines at frequencies $\omega = n\Omega$ with $n \in [1, 2, 3]$ will be observed in order E^2 and $\hbar^2$, respectively. We compared this result with the original (and wrong) prediction due to Drude. He considered only part of the response of the helix to the external applied field, namely the components parallel to the axis of the helix, while neglecting the perpendicular component. We observed that the parallel component of optical activity is independent of both $\hbar$ and E and gives rise to a line in the circular dichroism spectrum at

the fundamental frequency Ω. On the other hand, the perpendicular component is strongly dependent on E and $\hbar$ and will be anharmonic in general. Only in the classical limit and at $E = 0$ the parallel and perpendicular component of optical activity will be of like magnitude but opposite sign, so that the total optical activity vanishes.

We also consider the possibility to study separately the contribution of these two components by taking into account an oriented sample of Drude helices as to be found e. g. in Langmuir Blodgett films of helicene derivatives [17, 18, 29]. These oriented samples form a bi-anisotropic system. The only case where optical rotation will be observed occurs when the light propagates parallel to the optical axis, which coincides with the axes of the helices. We predicted that the optical activity will not vanish in that case even in the classical limit at $E = 0$. Instead, the optical activity will become proportional to the oscillator strength describing electric dipole transitions. Thus we conclude that the vanishing of the isotropic optical activity in the classical limit at $E = 0$ is due to a delicate balance between the individual optical activities for different orientations of the axes.

In sec. IV we compared the Drude model with two other models describing one electron optical activity, namely the models of Condon, Altar, and Eyring [24] on the one hand and the model of Tinoco and Woody [25] on the other. While all three models are optically active, they show qualitatively different behavior, especially in the combined classical and low energy limit. In that limit, the model of Condon et al. is generical for systems of one electron moving in an analytical potential with unique equilibrium position. We found that the vanishing of optical activity in that limit is also due to the localization of the particle at the equilibrium position where it does not perceive the intrinsic chirality of the potential. However, as this model is truly three dimensional, the optical activity vanishes proportional to $\hbar$ and E while in the Drude model, with its one-dimensional potential which is not an analytic function of $\mathbf{x}$, optical activity vanishes like $\hbar^2$ and E^2. Finally, the model of Tinoco and Woody, which describes the free motion of a particle on a helix, is qualitatively different from the other two models considered as there is no designated equilibrium position. We found that due to this difference in the classical limit the spectrum does not vanish as a function of E but remains invariant if the frequency is measured in units of the natural

frequency of the system, $\Omega(E)$, which itself is proportional to $\sqrt{E}$.

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